

## Learning Check

- 1. A** Your friend Juno says that if you close all windows, doors, and vents in a parked car on a hot day, the inside of the car will stay cool because no hot air can get in. Using the second law of thermodynamics, explain why Juno's reasoning is faulty.  

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- 2. C** A sample of water freezes, releasing 23.5 kJ of heat to the surroundings. If the same sample of water were to melt, how much heat would be absorbed by the system? Explain your answer.  

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- 3. A** One type of cold pack is made up of two pouches. One contains water and the other contains ammonium nitrate. To activate the cold pack, you squeeze the outer package, breaking the inner pouches and allowing the water and ammonium nitrate to mix. The pack becomes very cold as the ammonium nitrate dissolves.
  - a.** What type of enthalpy change is involved here? 

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  - b.** Is this an endothermic or exothermic process? 

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  - c.** Which has a greater total enthalpy: the original bonds existing in the ammonium nitrate salt and the water, or the bonds that form between the solute and solvent as the ammonium nitrate dissolves?  

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## Study Tip

Use this mnemonic to help you remember the difference between exothermic and endothermic processes: In an **ex**othermic process, heat **ex**its the system. In an **en**dothermic process, heat **en**ters the system.

## Enthalpy Changes and Chemical Reactions (5.2)

The enthalpy changes in chemical reactions are due to the changes in energy that result when chemical bonds are broken and formed.

- Breaking bonds requires energy and is therefore an endothermic process.
- Forming bonds releases energy and is therefore an exothermic process.

The difference between the energy required to break the bonds in the reactants and the energy released when the bonds in the products form is equal to the overall energy change for a given reaction.

## Thermochemical Equations and Enthalpy Diagrams (5.2)

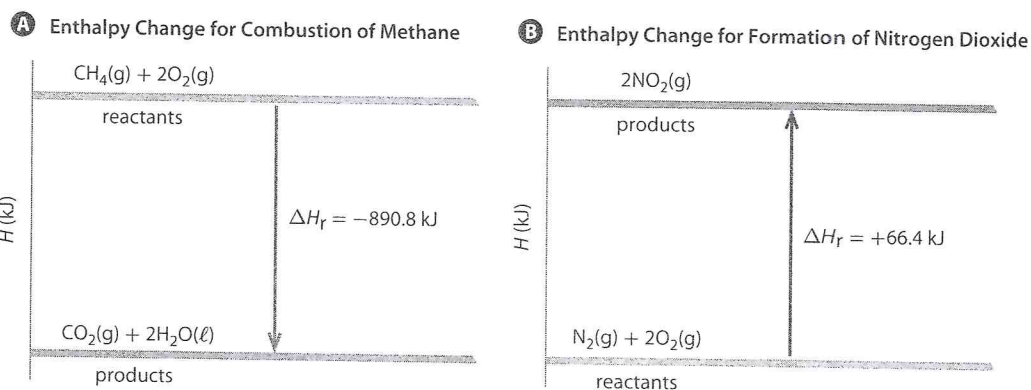
When a process takes place under conditions of constant pressure, the enthalpy change of a system is equal to the amount of heat that the system gains or loses. A thermochemical equation that describes a chemical reaction includes the value for the enthalpy change of the reaction. There are two commonly used ways to write thermochemical equations, as shown in the table on the next page.

### Examples of Thermochemical Equations

Reaction Type	Sample Thermochemical Equations	Notes
exothermic	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 890.8 \text{ kJ}$	For an exothermic reaction, the enthalpy change may either be written as part of the products or as a $\Delta H_r$ term written to the right of the equation. Note the negative sign when the enthalpy is written as a separate term to show that the reaction is exothermic.
	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$ $\Delta H_r = -890.8 \text{ kJ}$	
endothermic	$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) + 66.4 \text{ kJ} \rightarrow 2\text{NO}_2(\text{g})$	For an endothermic reaction, the enthalpy change may either be written as part of the reactants or as a $\Delta H_r$ term written to the right of the equation. Note the positive sign when the enthalpy is written as a separate term to show that the reaction is endothermic.
	$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ $\Delta H_r = +66.4 \text{ kJ}$	

The enthalpy changes given in a thermochemical equation of either type are for *stoichiometric quantities of the reactions as written in the equation*. For example, for the exothermic reaction shown above, 890.8 kJ of heat is released when 1 mol of methane and 2 mol of oxygen react to produce 1 mol of carbon dioxide and 2 mol of water. A reaction involving larger or smaller amounts of substances would result in a different enthalpy change.

Enthalpy diagrams show the relative enthalpies of the reactants and products and whether the reaction is exothermic or endothermic. In exothermic reactions, such as that represented in **A**, below, the products are drawn below the reactants because their enthalpy is lower. In an endothermic reaction such as that represented in **B**, below, the products have a higher enthalpy, so they are drawn above the reactants.

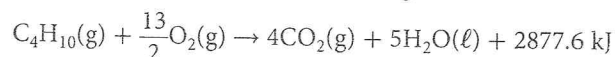


Enthalpy diagrams for exothermic (**A**) and endothermic (**B**) reactions.

### Notes on Notation

The enthalpy changes for various reactions have been well studied and can be found in tables in your textbook and elsewhere. Pay attention to the notation, however, to be sure what enthalpy change is being listed, and under what conditions. For example:

- The standard enthalpy of a reaction as written ( $\Delta H_r^\circ$ ) is the enthalpy change for the reaction that occurs with amounts of reactant and product determined by the coefficients in the chemical equation under standard conditions.
- The standard molar enthalpy of combustion ( $\Delta H_{\text{comb}}^\circ$ ) of a compound is the enthalpy change that occurs when 1 mol of a compound undergoes complete combustion with oxygen under standard conditions. For example,  $\Delta H_{\text{comb}}^\circ$  for butane,  $\text{C}_4\text{H}_{10}(\text{g})$ , is  $-2877.6 \text{ kJ/mol}$ . This can be written as the following thermochemical equation:



## Using Thermochemical Equations to Determine Enthalpy Changes (7.1)

The enthalpy of a reaction is directly proportional to the amounts of the substances that react. (For example, if the amounts of products and reactants involved in a reaction are doubled, the associated enthalpy change will also double.) Therefore, you can use stoichiometric techniques to analyze the enthalpy changes involved in chemical reactions. Work through the following sample problems for some examples of how to do this.

### Sample Problem: Calculating an Enthalpy Change

#### Problem

What is the enthalpy change when a 35.00 g sample of pentane undergoes complete combustion according to the equation  $\text{C}_5\text{H}_{12}(\ell) + 8\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$ ?  $\Delta H_{\text{comb}}$  for pentane is  $-3509.0 \text{ kJ/mol}$ .

#### What Is Required?

You need to determine the enthalpy change when 35.00 g of pentane combusts.

#### What Is Given?

You are given the mass of pentane:  $m =$  \_\_\_\_\_

You are given the balanced chemical equation: \_\_\_\_\_

You know the  $\Delta H_{\text{comb}}$  for pentane: \_\_\_\_\_

Plan Your Strategy	Act on Your Strategy
Determine the amount of pentane by using its mass and its molar mass.	$n = \frac{m}{M}$ $= \frac{35.00 \text{ g}}{72.15 \text{ g/mol}}$ $=$
Multiply the standard molar enthalpy of combustion by the amount of pentane to determine the enthalpy change associated with the combustion of 35.00 g of pentane.	$\Delta H = n\Delta H_{\text{comb}}^{\circ}$ $=$ mol ( _____ kJ/mol) $=$

#### Check Your Solution

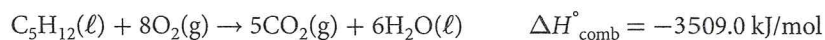
Check that the units are correct. A hydrocarbon combustion reaction is always exothermic, so the sign of the enthalpy change should be negative. About 0.5 mol of pentane was combusted, so the enthalpy change should be about one-half the standard molar enthalpy of combustion.



## Sample Problem: Using Enthalpy Data to Determine the Mass of Products

### Problem

When pentane undergoes complete combustion, heat is released and oxygen is consumed. Determine the mass of oxygen consumed if the enthalpy change of the reaction is  $-2.50 \times 10^2$  kJ.



### What Is Required?

You need to determine the mass of oxygen consumed in a reaction in which the total enthalpy change is  $-2.50 \times 10^2$  kJ.

### What Is Given?

You know the chemical equation for the reaction: \_\_\_\_\_

You know that for pentane,  $\Delta H_{\text{comb}} =$  \_\_\_\_\_

You also know the total enthalpy change for the given reaction  $\Delta H_r =$  \_\_\_\_\_

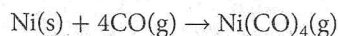
Plan Your Strategy	Act on Your Strategy
Determine the amount in moles of pentane combusted, using this formula $\Delta H_r = n\Delta H^\circ_{\text{comb}}$	$\Delta H_r = n\Delta H^\circ_{\text{comb}}$ $n = \frac{\Delta H_r}{\Delta H^\circ_{\text{comb}}}$ $= \frac{\text{kJ}}{\text{kJ/mol}}$ $=$
Determine the amount in moles of oxygen consumed from the ratio of coefficients and the calculated amount in moles of pentane combusted.	$\frac{n_{\text{O}_2}}{n_{\text{C}_5\text{H}_{12}}} = \frac{n_{\text{O}_2 \text{ consumed}}}{n_{\text{C}_5\text{H}_{12} \text{ consumed}}}$ $\frac{8 \text{ mol O}_2}{1 \text{ mol C}_5\text{H}_{12}} = \frac{n_{\text{O}_2 \text{ consumed}}}{\text{mol C}_5\text{H}_{12}}$ $n_{\text{O}_2 \text{ consumed}} = \left( \frac{8 \text{ mol O}_2}{1 \text{ mol C}_5\text{H}_{12}} \right) \text{ mol C}_5\text{H}_{12}$ $=$
Determine the mass of oxygen consumed by using its molar mass and its amount in moles.	$n = \frac{m}{M}$ $m = nM$ $= \text{mol O}_2 (32.00 \text{ g/mol})$ $=$

### Check Your Solution

Check that the units are correct. The mass of oxygen consumed should be less than the mass of 8 mol  $\text{O}_2(\text{g})$ , which is 256 g, because the enthalpy change of the reaction is less than  $\Delta H^\circ_{\text{comb}}$ .

## Learning Check

1. **T/I** Consider the following chemical reaction.



This reaction as written has an enthalpy change of  $-159.6 \text{ kJ}$ .

- a. Write this information as thermochemical equations in two different ways.

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- b. What is meant by “as written?”

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- c. If 2 mol Ni(s) react completely in excess carbon monoxide according to the equation above, what enthalpy change would you expect?

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- d. State the relationship between the enthalpy of a reaction and the quantity of substances involved.

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2. **C** Consider the reaction represented by the following thermochemical equation.



- a. Draw an enthalpy diagram for the reaction.

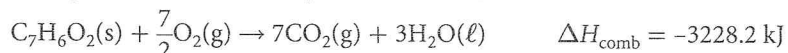
- b. Which process involves a greater enthalpy change: the breaking of the bonds in the reactants or the formation of the bonds in the products? Explain your answer.

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3. **T/I** The complete combustion of benzoic acid,  $\text{C}_7\text{H}_6\text{O}_2(\text{s})$ , is represented by the following balanced chemical equation.



- a. If a sample of benzoic acid undergoes complete combustion, releasing  $-9684.6 \text{ kJ}$  of energy, what mass of  $\text{C}_7\text{H}_6\text{O}_2(\text{s})$  is combusted in the reaction?

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- b. If 25.0 mol of oxygen are consumed in the complete combustion of a sample of benzoic acid, what is the enthalpy change?

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## Study Tip

Use the techniques of stoichiometry that you learned in Grade 11 Chemistry to analyze thermochemical equations.